

Claims:

1. A composite of a vulcanizable rubber or rubber-type composition having at least one metal reinforcement element embedded therein, wherein said metal reinforcement elements have a coating of a polymer deposited from a solution and are compatible with and co-polymerizable with said vulcanizable rubber composition, and bearing functional groups covalently bonding to the metal surface of said reinforcement element.

2. A composite according to claim 1, wherein said solution is an aqueous solution.

3. A composite according to claim 1, wherein said solution is an alcoholic solution.

4. A composite according to claim 1, wherein said solution is an organic solution.

5. A composite according to claim 1, wherein said metal reinforcement elements have a coating of a non-cured rubber composition.

6. A composite according to claim 1, wherein said metal reinforcement elements are co-vulcanizable with said vulcanizable rubber composition.

7. A composite according to claim 1, wherein said metal reinforcement elements are crosslinkable with said vulcanizable rubber composition.

8. A composite according to claim 1, wherein said functional groups form covalent bonds with the outward directed first functional groups of a molecular layer of a bifunctional adhesion promoter which is intercalated between said metal reinforcement elements and said coating and is bound to said metal reinforcement elements by its second functional groups.

9. A composite according to claim 1, wherein said metal reinforcement elements comprise on top of said coating, a layer of a skim composition for the vulcanizable rubber or rubber-like composition.

10. A composite according to claim 1 wherein the vulcanizable rubber composition to be reinforced is a composition selected from the group consisting of a synthetic poly(isoprene), a natural poly(isoprene), a synthetic poly(butadiene), natural poly(butadiene), a styrene-butadiene-rubber (SBR), a halobutylrubber, or an ethylene-propylene-diene-rubber (EPDM).

11. A composite according to claim 1, wherein said metal reinforcement element is an elongated steel element.

12. A composite according to claim 11, wherein said elongated steel element is coated with at least one metallic layer.

13. A composite according to claim 12, wherein said metallic layer is comprised of a metal selected from the group consisting of brass, bronze, zinc, zinc alloy, tin or tin alloy.

14. A composite according to claim 13, wherein said zinc alloy is an alloy selected from the group consisting of a zinc-aluminium alloy, a zinc-aluminium-mischmetal alloy, a zinc-manganese alloy, a zinc-cobalt alloy, a zinc-nickel alloy, a zinc-iron alloy or a zinc-tin alloy.

15. A composite according to claim 5, wherein said non-cured rubber composition is comprised of matter selected from the group consisting of a synthetic poly(isoprene), a natural poly(isoprene), a synthetic poly(butadiene), a natural poly(butadiene), a synthetic elastomer or a thermoplastic elastomer.

16. A composite according to claim 1 wherein said polymer bonds directly to the metal surface and has functional groups selected from the group consisting of:

- 10 thiol groups, mercapto groups, silanes, amines,
 -SH; -SiHCl₂; -SiH₂Cl; -Si(Cl)₃; -SiHBr₂; -SiH₂Br; -SiBr₃; -Si(R'(Cl)₂);
 -Si(OR')₃; -Si(R'(OR')₂); -COOH; -COCl;
 -PO₃H₂, -SO₂H,
 acid anhydrides of -SH; -SiHCl₂; -SiH₂Cl; -Si(Cl)₃; -SiHBr₂; -SiH₂Br; -
 15 SiBr₃; -Si(R'(Cl)₂); -Si(OR')₃; -Si(R'(OR')₂); -COOH; -COCl;
 -PO₃H₂, -SO₂H,
 acid chloride groups of -SH; -SiHCl₂; -SiH₂Cl; -Si(Cl)₃; -SiHBr₂; -SiH₂Br;
 -SiBr₃; -Si(R'(Cl)₂); -Si(OR')₃; -Si(R'(OR')₂); -COOH; -COCl;
 -PO₃H₂, -SO₂H,
 20 organometallic groups of the formula -M(OR')_n, whereby M is a metal
 selected from the group consisting of Al, Sn, B, Ti and V; and n is the ligand
 number corresponding to the metal M; and
 a phthalocyanin, phthalonitril groups, a monothiol, or monothiolate groups;
 and R' is an alkyl selected from the group consisting of methyl, ethyl or
 25 propyl.

17. A composite according to claim 1 wherein said polymer bonds to the intercalated adhesion promoter and has functional groups comprising thiol groups, mercapto groups, silanes, amines,

-SH; -SiHCl₂; -SiH₂Cl; -Si(Cl)₃; -SiHBr₂; -SiH₂Br; -SiBr₃; -Si(R'(Cl)₂);

5 -Si(OR')₃; -Si(R'(OR')₂); -COOH; -COCl;

-PO₃H₂, -SO₂H,

acid anhydride groups of -SH; -SiHCl₂; -SiH₂Cl; -Si(Cl)₃; -SiHBr₂; -SiH₂Br; -SiBr₃; -Si(R'(Cl)₂); -Si(OR')₃; -Si(R'(OR')₂); -COOH; -COCl;

-PO₃H₂, -SO₂H,

10 acid chloride groups of -SH; -SiHCl₂; -SiH₂Cl; -Si(Cl)₃; -SiHBr₂; -SiH₂Br; -SiBr₃; -Si(R'(Cl)₂); -Si(OR')₃; -Si(R'(OR')₂); -COOH; -COCl;

-PO₃H₂, -SO₂H,

a phthalocyanin, phthalonitril groups, a monothiol, or monothiolate groups;

wherein R' is an alkyl selected from the group consisting of methyl, ethyl

15 or propyl; and

said functional groups are terminal groups.

18. A composite according to claim 17, wherein said functional groups are carried along a polymer backbone.

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19. A composite according to claim 17, wherein said functional groups are part of side chains of the polymer.

20. A composite according to claim 18, wherein said functional groups are epoxy groups carried along the polymer backbone.

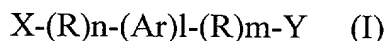
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21. A composite according to claim 18, wherein said functional groups are epoxy groups which are part of side chains attached to the polymer backbone.

22. A composite according to claim 16, wherein said organometallic groups are of the formula $-M(Cl)_n$,

23. A composite according to claim 5, wherein said non-cured rubber composition comprises common vulcanization additives and curing systems.

24. A composite according to claim 1, wherein said polymer is bound to said metal surface by an adhesion promoter that is a bifunctional compound of the general formula (I)



with x representing a group capable of reacting covalently at the metal surface,

R representing an organic spacer chain,

Ar representing an aromatic system,

Y representing a group capable of forming covalent bonds to the functional groups of said coating, and $0 \leq n, m \leq 16$; and $0 \leq l \leq 6$.

25. A composite according to claim 24, wherein A represents a heteroaromatic system.

26. A composite according to claim 24 wherein

X is a functional group selected from the group consisting of -SH; $-\text{SiHCl}_2$; $-\text{SiH}_2\text{Cl}$; $-\text{Si}(\text{Cl})_3$; $-\text{SiHBr}_2$; $-\text{SiH}_2\text{Br}$; $-\text{SiBr}_3$; $-\text{Si}(\text{R}'(\text{Cl})_2)$; $-\text{Si}(\text{OR}')_3$; $-\text{Si}(\text{R}'(\text{OR}')_2)$; $-\text{COOH}$; $-\text{COCl}$; $-\text{PO}_3\text{H}_2$; $-\text{SO}_2\text{H}$; an organometallic group of the formula $-M(\text{OR}')_n$, whereby M is a metal selected from the group consisting of Al, Sn, B, Ti and V and n is the ligand number corresponding to the metal M; a phthalocyanin; a phthalonitril group; a monothiol; or a monothiolate group;

R' is an alkyl

Y is a functional group selected from the group consisting of NH_2 ; NHR' ; NR'_2 ; an unsaturated residue; an acrylic acid group; a methacrylic acid group; methyl esters or ethyl esters;

-CN is a functional group selected from the group consisting of an
 5 activated carboxylic ester; an aldehyde group; an epoxide group; -SH; $-\text{SiHCl}_2$; $-\text{SiH}_2\text{Cl}$; $-\text{Si}(\text{Cl})_3$; $-\text{SiHBr}_2$; $-\text{SiH}_2\text{Br}$; $-\text{SiBr}_3$; $-\text{Si}(\text{R}'(\text{Cl})_2)$; $-\text{Si}(\text{OR}')_3$; $-\text{Si}(\text{R}'(\text{OR}')_2)$; $-\text{COOH}$; $-\text{COCl}$; or a functional group capable of forming a complex with at least one ingredient of a non-metallic medium;

R represents $-\text{CH}_2-$; and

10 AR represents an aromatic system.

27. A composite according to claim 26, wherein AR represents a heteroaromatic system.

15 28. A composite according to claim 26, wherein R represents a $-(\text{CH}_2)-$ chain; $2 \leq n \leq 20$; and said chain may be unhalogenated, may contain aromatic units, and may comprise constituents selected from the group consisting of: $-(\text{CH}_2)_i\text{CH}_3$ where $0 \leq i \leq 5$, $-\text{O}(\text{CH}_2)_j\text{CH}_3$, or $-\text{O}(\text{CF}_2)_j\text{CH}_3$ where $0 \leq j \leq 4$, -CN and $-\text{NH}_2$; $-\text{CF}_2-$; $-\text{CH}_2-\text{CO}-\text{NH}-\text{CH}_2-$; $-\text{CF}_2-\text{CO}-\text{NH}-\text{CF}_2-$; $-\text{CH}_2-\text{CO}-\text{NH}-\text{CF}_2-$;
 20 $-\text{CF}_2-\text{CO}-\text{NH}-\text{CH}_2-$ where $0 \leq n$ and $m \leq 16$.

29. A composite according to claim 28, wherein said chain may be partially halogenated.

25 30. A composite according to claim 28, wherein said chain may be perhalogenated.

31. A composite according to claim 28, wherein said chain may contain thiophen units.

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32. A composite according to claim 28, wherein said aromatic units may comprise constituents selected from the group consisting of: $-(CH_2)_iCH_3$ where $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$, or $-O(CF_2)_iCH_3$ where $0 \leq j \leq 4$, $-CN$ and $-NH_2$; $-CF_2-$; $-CH_2-CO-NH-CH_2-$; $-CF_2-CO-NH-CF_2-$; $-CH_2-CO-NH-CF_2-$; $CF_2-CO-NH-$
 5 CH_2- where $0 \leq n$ and $m \leq 16$.

33. A composite according to claim 31, wherein said thiophen units may comprise constituents selected from the group consisting of: $-(CH_2)_iCH_3$ where $0 \leq i \leq 5$, $-O(CH_2)_jCH_3$, or $-O(CF_2)_iCH_3$ where $0 \leq j \leq 4$, $-CN$ and $-NH_2$; $-CF_2-$; $-$
 10 $CH_2-CO-NH-CH_2-$; $-CF_2-CO-NH-CF_2-$; $-CH_2-CO-NH-CF_2-$; $CF_2-CO-NH-CH_2-$ where $0 \leq n$ and $m \leq 16$.

34. A composite according to claim 26, wherein X is a functional group selected from the group consisting of the acid anhydride group of $-SH$; $-SiHCl_2$; $-$
 15 SiH_2Cl ; $-Si(Cl)_3$; $-SiHBr_2$; $-SiH_2Br$; $-SiBr_3$; $-Si(R'(Cl)_2)$; $-Si(OR')_3$; $-Si(R'(OR')_2)$; $-COOH$; $-COCl$; $-PO_3H_2$, or $-SO_2H$.

35. A composite according to claim 26, wherein X is a functional group selected from the group consisting of the acid chloride group of $-SH$; $-SiHCl_2$; $-$
 20 SiH_2Cl ; $-Si(Cl)_3$; $-SiHBr_2$; $-SiH_2Br$; $-SiBr_3$; $-Si(R'(Cl)_2)$; $-Si(OR')_3$; $-Si(R'(OR')_2)$; $-COOH$; $-COCl$; $-PO_3H_2$, or $-SO_2H$.

36. A composite according to claim 26, wherein R' is an alkyl selected from the group consisting of methyl, ethyl or propyl.

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37. A composite according to claim 26, wherein said organometallic group is of the formula $-M(Cl)_n$.

38. A cured rubber or rubber-like composition obtained by
 30 vulcanization of a composite according to claim 1.

39. A composition according to claim 38, wherein said composition is a pneumatic tire.

5 40. A composition according to claim 38, wherein said composition is a hose.

41. A composition according to claim 38, wherein said composition is a conveyor belt.

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42. A composition according to claim 38, wherein said composition is a pulley belt.

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